

Stability of Metallic Structure in Compressed Solid GeH₄

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We study the electronic and lattice dynamical properties of compressed solid germane in the pressure range up to 200 GPa with density functional theory. A stable metallic structure, *Aba2*, with a base-centered orthorhombic symmetry was found to be the lowest enthalpy phase for pressure from 23 to 177 GPa, suggesting an insulator to metal phase transition around 23 GPa. The *Aba2* structure is predicted to have higher superconducting transition temperature than SiH₄ reported recently, thus presenting new possibilities for exploring high temperature superconductivity in this hydrogen-rich system.

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As suggested by Ashcroft [1], the dense hydrides of group IVa elements (C, Si, Ge, and Sn) are promising candidates for realizing metallization of solid hydrogen because hydrogen has already been “chemically precompressed”. The metallization pressures in the group IVa hydrides are believed to be considerably lower than may be necessary for solid hydrogen. Ashcroft [1] also suggested that these hydrogen-rich alloys are likely superconductors with high transition temperatures T_c . As put by Ginzburg [2], “high-temperature and room-temperature superconductivity” and “metallic hydrogen and other exotic substances” are the two key “physical minima” at the beginning of the 21st century. Thus, exploring the possibility of metallic hydrogen and superconductivity has long been a major driving force in high-pressure condensed matter science and remains an important challenge in modern physics. Recent experimental work on SiH₄, using diamond-anvil cell techniques, has revealed an enhanced reflectivity with increasing pressure [3]. It was found [3] that solid SiH₄ becomes opaque at 27-30 GPa and exhibits Drude-like behavior at around 60 GPa, signalling the onset of pressure-induced metallization. After Chen’s experiment, Eremets et al reported that SiH₄ exhibits superconductivity at 96 and 120 GPa[4].

Prior to the experiment of Chen [3], several theoretical studies on SiH₄ structure addressed the issue of whether the material is a favorable candidate of high temperature superconductor. For a metallic *Pman* SiH₄ phase, Feng *et al* [5] obtained a superconducting transition temperature T_c of 166 K at 202 GPa by using the electron-phonon coupling strength for lead under ambient pressure. Pickard and Needs [6] also studied the structural properties of SiH₄ and mentioned the possibility of superconductivity in a *C2/c* phase. Later, Yao *et al.* [7] showed that the *Pman* structure is in reality not stable and that a new *C2/c* structure is dynamically stable from 65 to 150 GPa. This *C2/c* SiH₄ phase was predicted to exhibit

superconductivity close to 50 K at 125 GPa [7]. Recently, Chen *et al.* [8] carried out first principles calculations on SiH₄ to obtain structural, electronic, and vibrational information, and they found out six energetically favorable structures in which the $P\bar{1}$, *Cmca*, and *C2/c* structures have layered networks with eight-fold SiH₈ coordination. This layered feature favors metallization and were predicted to have T_c in the range of 20 and 80 K.

Compare to SiH₄, there exist very few theoretical studies and almost none experimental work was done on germane. Recent progress on SiH₄ make it profitable to perform high pressure studies on GeH₄. In early *ab initio* studies of GeH₄, Martinez et al [9] found that at around 72 GPa the metallic SnF₄-like structure becomes preferred. Li et al [10] followed studies of Feng *et al* on SiH₄ [5] and investigated a few possible structures. They found that T₂ and O₃ could be metallic under pressure. It is not known whether there exists a common structural feature that favors metallic GeH₄, and no study on the possible superconductivity has been attempted.

In this Letter we report a theoretical study of metallic phases and possible superconductivity in compressed solid GeH₄. Considering the fact that germanium has a small band gap than silicon, GeH₄ is expected to become metallic easier than SiH₄. By calculating possible structures of different crystal systems including monoclinic, orthogonal, tetragonal, hexagonal, and cubic structures, we found five energetically favorable structures in which the *C2/c*, *Aba2*, and *Ccca* structures have layered networks. This layered feature favors metallization and superconductivity. The *Aba2* phase is predicted to have considerable higher superconducting transition temperature T_c at lower pressure (<50 GPa), suggesting that GeH₄ is another good candidate for high-temperature superconductivity.

To study the structural and electronic behavior of GeH₄ over a wide range of the pressure, we used generalized gradient approximation (GGA) density functional

and projector augmented wave method as implemented in the Vienna ab initio simulation package (VASP) [11]. An energy cutoff of 540 eV was used for the plane wave basis sets, and $16 \times 16 \times 16$ and $8 \times 8 \times 8$ Monkhorst-Pack k -points grids were used for Brillouin zone sampling of two GeH_4 molecular cells and four GeH_4 molecular cells, respectively. When searching stable structures, we performed calculations with relaxation of cell volume, cell shape, and ionic positions. Forces on the ions were calculated through derivatives of the free energy with respect to the atomic positions, including the Harris-Foulkes like correction. Iterative relaxation of atomic positions was stopped when all forces were smaller than 0.01 eV/\AA . All possible structures were optimized using conjugate gradient scheme. The lattice dynamical and superconducting properties were calculated by the Quantum-Espresso package [12] using Vanderbilt-type ultrasoft potentials with a cut-off energy of 30 Ry and 300 Ry for the wave functions and the charge density, respectively. $24 \times 12 \times 24$ Monkhorst-Pack k -point grid with Gaussian smearing of 0.05 Ry was used for the phonon calculations. Double k -point grids were used for calculation of the electron-phonon interaction matrix element.

The phase stability of GeH_4 was systematically investigated by means of first-principles total energy calculations. Dozens of the selective structures were selected as the initial structures, which cover all the competing structures of SiH_4 in previous literatures.[5, 6, 7, 8] It is worthy noting that $I4_1/a$ structure, a most stable phase over a wide pressure range (60-240 GPa) in SiH_4 , is unstable in the whole pressure range we studied. Five low-enthalpy structures of GeH_4 , i.e., *Aba2*, *Ccca*, $P2_1/c$, *C2/c*, and *Fdd2*, were found for pressure up to 200 GPa. Enthalpy differences as a function of pressure for five competing structures are plotted in Fig. 1. Three regions are clearly seen by our calculation: (i) 0-23 GPa, two monoclinic phases, *Fdd2* and $P2_1/c$ dominate; (ii) 23-177 GPa, it is *Aba2*, an orthorhombic phase; (iii) 177-200 GPa, it is monoclinic *C2c*. For germane, it is at about 23 GPa that an insulator to metal transformation occurs.

Near the pressure of 2 GPa, numerous structures with monoclinic tetrahedral or orthorhombic symmetry, have very close enthalpy, constituting a “mixed” phase of GeH_4 (see auxiliary material), which reflects the combined effect of exerted force and van der Waals force. Among them, two structures, one with *Fdd2* symmetry and the other one with $P2_1/c$, seem to be more stable. The two structures are very close in enthalpy as shown in the inset of Fig. 1. The *Fdd2* phase is a face-centered orthorhombic structure composed of eight four-fold coordinated tetrahedra. The eight GeH_4 molecules in the unit cell are comparable and similarly ordered, so that the neighboring molecules are kept apart. With the increasing of pressure, the distance between Ge atoms decreases. Consequently, the shape of the whole cell changes and it results in the more stable $P2_1/c$ phase. The $P2_1/c$ structure consists of four isolated covalently bonded GeH_4

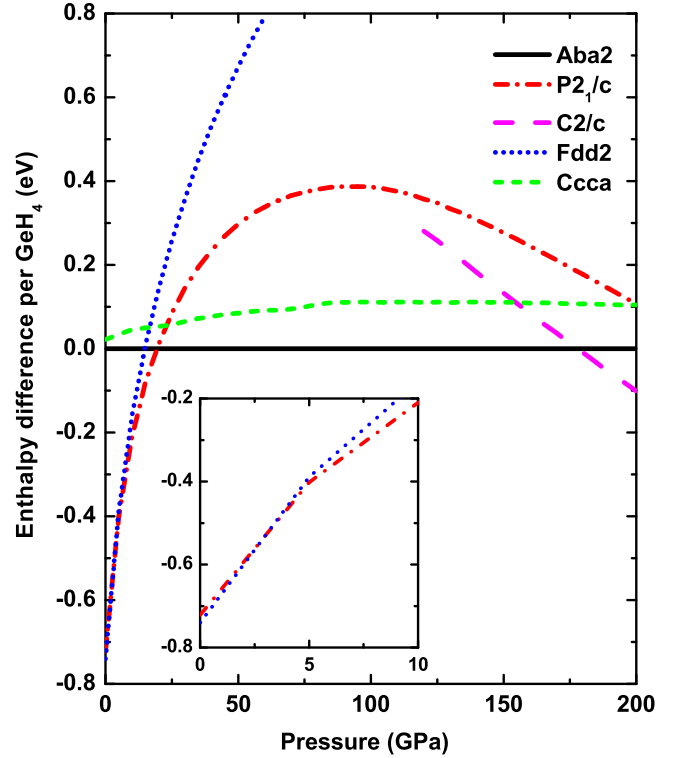


FIG. 1: (color online) The enthalpy versus pressure for five competitive structures of GeH_4 . The enthalpy of the *Aba2* phase is taken as the reference point. The inset shows enthalpy difference between *Fdd2* and $P2_1/c$.

tetrahedra with the H atom of one molecule pointing away from the H atoms of a neighboring molecule. Due to the symmetry, the arrangement of GeH_4 tetrahedra in the *Fdd2* structure is more orderly than the $P2_1/c$ structure. The Ge atoms in the *Fdd2* phase forms quasi-two-dimensional sheets, while the H atoms are “fastened” by the Ge atoms. This makes it transform to other layered structures more easily. The Ge-H bond lengths of these two structures are similar (1.53 \AA), leading to small difference in their unit volume. Subsequently, the transformation between them is very likely to occur in this pressure region. Because of the covalently bonded GeH_4 , it is not surprising that these two structures are insulating in this pressure range, and they were also found in the low-pressure SiH_4 . [8] The *Fdd2* phase wins for pressure below 5 GPa, while the $P2_1/c$ phase takes over for pressure ranges from 5 to 23 GPa. The occurrence of mixed phases indicates that it is difficult to verify the structure of GeH_4 at very low pressure (about 3 GPa) from experiments.

Around 20 GPa, *Fdd2* and $P2_1/c$ are also energetically competitive, along with two new layered phases, *Aba2* and *Ccca*. These four structures compete drastically over the pressure range from 14 to 23 GPa for low enthalpy phase. The maximum enthalpy difference between them is only 0.05 eV, indicating that solid GeH_4

undergoes a structure transition in this pressure range. Our calculations showed that the orthorhombic $Fdd2$ structure transforms to other two orthorhombic structures with $Aba2$ and $Ccca$ symmetry at 14 GPa and 16 GPa, respectively. Compared with $Fdd2$, the transition from monoclinic $P2_1/c$ phase to $Aba2$ and $Ccca$ needs more pressure. $P2_1/c$ transforms to $Aba2$ structure at 20 GPa and to $Ccca$ structure at 23 GPa. It is interesting to note that $Ccca$ structure transforms to $P2_1/c$ at high pressure (about 200 GPa) again.

As shown, the most stable phase found in a wide pressure range (23 to 177 GPa) is a layered base-centered orthorhombic structure of space group $Aba2$. This is remarkably different from the case of SiH_4 , where metallic phases ($C2/c$, $Cmca$, $P\bar{1}$, etc.) are higher in enthalpy than insulating phases for pressure lower than 200 GPa. For the $Aba2$ structure there are four formula units per unit cell. Four Ge atoms hold the Wyckoff $4a$ sites and 16 H atoms occupy two Wyckoff $8b$ sites. The adjacent Ge layers are bridged by a pair of H atoms with Ge-H bond length from 1.935 Å (20 GPa) to 1.673 Å (175 GPa). The in-plane Ge-Ge bond length varies from 2.552 to 2.206 Å. The calculated density for the $Aba2$ structure at 50 GPa is 5.397 g/cm³. The most peculiar feature of this structure is the exceptionally short H-H bond length about 0.785 Å from 20 GPa to 175 GPa, nearly retaining the same. The paired hydrogen atoms occupy the Ge layers with different orientation. When pressure increases, the orientation of paired hydrogen changes.

A few words commenting on the $Ccca$ phase are in order. This structure has been discussed by Yao *et al* in their study of SiH_4 [7]. For GeH_4 , we found that $Ccca$ phase is also a layered structure and is a good metal at the same pressure range as the $Aba2$ phase. The enthalpy difference in $Ccca$ and $Aba2$ is very small (0.11 eV at most) at a large pressure range, 0 to 200 GPa. The $Aba2$ structure is about 0.053 eV per GeH_4 unit lower in enthalpy than the $Ccca$ structure at 20 GPa and about 0.11 eV at 177 GPa, respectively. The $Ccca$ structure contains four GeH_4 units per unit cell. The hydrogen atoms between Ge layers connect the Ge and form 2D layers itself, which is parallel to Ge layers. Both $Aba2$ and $Ccca$ structures are good candidates for metallic phases in this pressure region.

Upon further compression, the metallic $C2/c$ phase possesses the lowest enthalpy between 177 to 200 GPa. The $C2/c$ structure transforms to the $Ccca$ structure and the $Aba2$ structure at 154 GPa and 177 GPa, respectively. The $C2/c$ phase is also a layered structure which belongs to monoclinic crystal system. The present $C2/c$ structure is constructed by the two-dimensional Ge layers bridged by H atoms, and it is different from the $C2/c$ structure proposed by Pickard and Needs[6] when searching for the low-enthalpy structure of SiH_4 . Solid SiH_4 also prefers to have this structure at high pressure [8]. It is instructive to observe that the obtained metallic structures with $Aba2$, $Ccca$ and $C2/c$ symmetry all have layered structures. These structures are composed of distinct 2D lay-

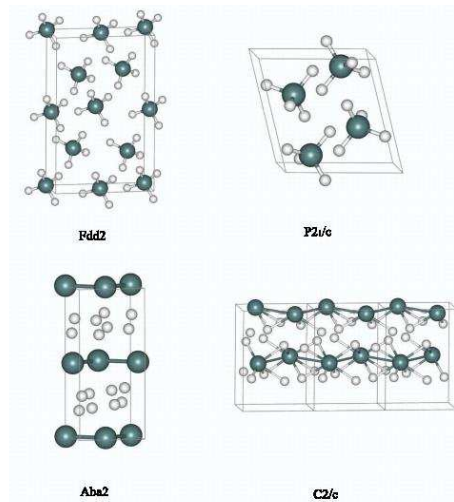


FIG. 2: (color online) The energetically most favorable structures computed for GeH_4 in the pressure range 0-200 GPa.

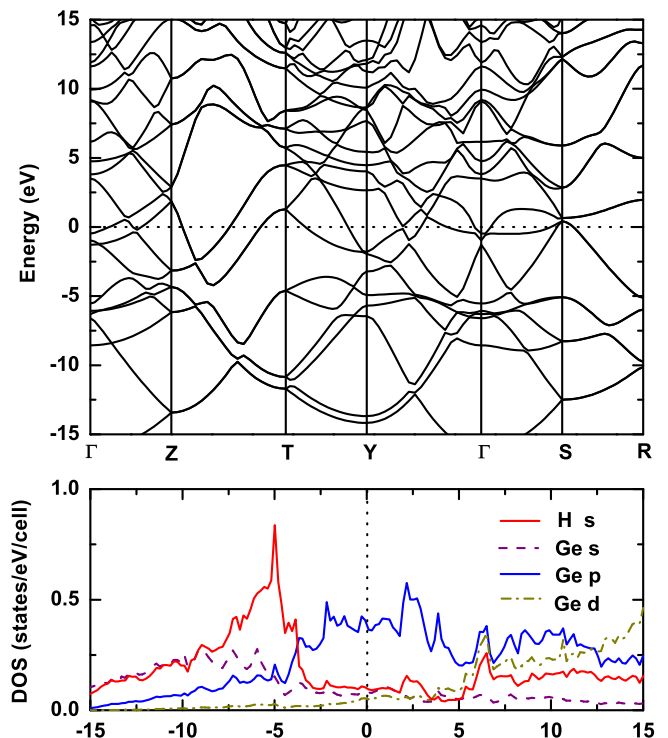


FIG. 3: (color online) Electronic band structure and density of states for the $Aba2$ phase of GeH_4 at the pressure of 30 GPa.

ers where the Ge atoms form a square-net bridged by H atoms. We thus obtained five energetically favorable structures for GeH_4 at high pressure. The atomic arrangements for the four structures are shown in Fig. 2. $Ccca$ structure is not given here since it has been discussed in SiH_4 by Yao *et al.*[7]

The energy band and density of states (DOS) of the $Aba2$ structure at 30 GPa pressure are shown in Fig. 3,

as an example. Electron structure presents two prominent features. One is that a strong hybridization between Ge-*p* electrons and H-*s* electron appears in valence and conduction bands from -15 to -5 eV and from 5 to 15 eV. The other one is that Ge atoms expand the coordination shell and use the 3*d* orbitals to bond with neighboring H atoms. This case is also observed in SiH₄ at high pressure.[7] The DOS at the Fermi level (N_F) for *Aba2* at 30 GPa attains a value of 1.1 (1.14 and 1.07 at 20 and 50 GPa, respectively) states/eV/cell, exhibiting its good metallic property. Dominant contributions to the DOS near the Fermi level come from Ge-*p* electrons. While Ge-*s*, Ge-*d*, and H-*s* have minor contributions to the DOS at the Fermi level. The band structure reveals metallic character with large dispersion bands crossing the Fermi level (E_F) and a flat band in the vicinity of E_F from the Γ to the *S* point. The simultaneous occurrence of flat and steep bands near the Fermi level has been suggested as favorable conditions for enhancing the electron pairing, which is essential to superconductivity.

Further, the possibility of superconductivity for *Aba2* structure of GeH₄ is discussed using the modified McMillan equation by Allen and Dynes.[13] For comparison, we calculate the T_c at 30 and 50 GPa. The obtained electron-phonon coupling parameters λ are 1.13 at 30 GPa and 1.37 at 50 GPa, which are higher than the predicted strong coupling value of 1.0[1], indicating a rather strong electron-phonon coupling (EPC) in GeH₄. This strong EPC is correlated to the wide valence band and strong electron-electron interaction along with interband electron transfer. Using the Coulomb pseudopotential μ^* of 0.1, 0.15, and 0.2, the estimated T_c are 26, 21, and 16 K at 30 GPa and 34, 28, and 23 K at 50 GPa, respectively. Though the DOS at Fermi level decrease with the pressure increasing, T_c increases. This can be under-

stood from the fact that the strengthen of EPC under pressure has advantage over the weaken of repulsion effects between electrons. All obtained T_c values in GeH₄ are comparable to the T_c value recently reported in SiH₄ at 96 and 120 GPa.[4] Most important is that no superconductivity was found in Eremets *et al*'s experiment for SiH₄ when the pressure is lower than 50 GPa.

In summary, we have investigated the structural stability of germane under pressure up to 200 GPa. The *Fdd2* phase is confirmed to be a good candidate for the low-pressure insulating phase. Between 5 and 23 GPa, *P2₁/c* is predicted to be the stable structure of another insulating phase. For a wide range of pressure, from 23 GPa to 177 GPa, the *Aba2* phase is confirmed to be the lowest in enthalpy. Calculations of band structure show that the *Aba2* phase is a metal even at zero pressure. Thus the transition pressure from insulator to metal is 23 GPa for germane, much lower than the theoretical metallization pressure of 50 GPa[4], 60 GPa[7], and 70 GPa[8] for silane. At higher pressures (above 177 GPa), germane transforms into another metallic structure with *C2/c* symmetry. The estimated superconducting critical temperatures for the metallic *Aba2* phase are comparative to those in SiH₄, making GeH₄ a potential superconductor.

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- [1] N. W. Ashcroft, Phys. Rev. Lett. **21**, 1748 (1968); *ibid* **92**, 187002 (2004).
 - [2] V. L. Ginzburg, Rev. Mod. Phys. **76**, 981 (2004).
 - [3] X. J. Chen, V. V. Struzhkin, Y. Song, A. F. Goncharov, M. Ahart, Z. X. Liu, H. K. Mao, and R. J. Hemley, Proc. Natl. Acad. Sci. U.S.A. **105**, 20 (2008).
 - [4] M. I. Eremets, I. A. Trojan, S. A. Medvedev, J. S. Tse, and Y. Yao, Science **319**, 1506 (2008).
 - [5] J. Feng, W. Grochala, T. Jaroń, R. Hoffmann, A. Bergara, and N. W. Ashcroft, Phys. Rev. Lett. **96**, 017006 (2006).
 - [6] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).
 - [7] Y. Yao, J. S. Tse, Y. Ma and K. Tanaka, Europhys. Lett. **78**, 37003 (2007).
 - [8] X. J. Chen, J. L. Wang, V. V. Struzhkin, H. K. Mao, and H. Q. Lin, arXiv:0803.2713.
 - [9] M. Martinez-Canales, A. Bergara, J. Feng, W. Grochala, Journal of Physics and Chemistry of Solids **67**, 2095 (2006).
 - [10] Z. Li, W. Yu and C. Q. Jin, Solid state Commu. **143**, 353 (2007).
 - [11] G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996).
 - [12] QUANTUM-ESPRESSO is a community project for high-quality quantum-simulation software, based on density-functional theory, and coordinated by Paolo Giannozzi. See <http://www.quantum-espresso.org> and <http://www.pwscf.org>
 - [13] P. B. Allen and R. C. Dynes, Phys. Rev. **12**, 905 (1975).